

15 JUL 2005

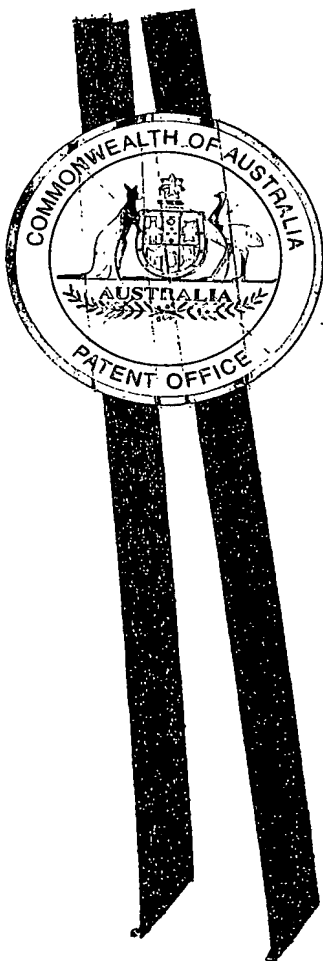


207542280
PCT/AU2004/000060

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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003901952 for a patent by IAN JACOBS as filed on 24 April 2003.



WITNESS my hand this
Thirtieth day of January 2004

J. Billingsley

JULIE BILLINGSLEY
TEAM LEADER EXAMINATION
SUPPORT AND SALES

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Title: Polymer blends with improved environmental stress crack resistance

DEFINITIONS

- **'255 patent** PCT/AU98/00255, which is incorporated by reference.
- **ACA:** 'additional compatible agent' which may be either a non-polymer or polymer which is compatible with the ALOP, ALOCA or ALOHMFCA. Materials capable of nucleating polymer crystallisation are typical and preferred ACAs.
- **ALOCA:** 'at-least-one-compatible-agent', which may be either a non-polymer or polymer which is compatible, but not miscible, with the ALOP and usually forms or is part of the disperse phase of a blend.
- **ALOHMFCA:** 'at-least-one-high-melt-flow-compatible-agent', which is an ALOCA polymer(s) having an MFI of >100 (eg. a 350 MFI PP). Particularly in the case of PP and EVAs, products with MFIs >100 may often be used interchangeably with their equivalent ALOCA.
- **ALOP:** 'at-least-one-polymer', which is usually the main polymer constituent(s) of a particular blend and is the polymer(s) forming the continuous phase of a blend. The ALOP has an MFI of >0.04 to >100 . The '255 patent contains many examples of ALOPs.
- **Blends:** Mixtures of one or more polymers that are suitable for use as blends of the present invention. The blends may be used 'as is', foamed by various means such as chemical blowing agents or subjected to post moulding treatments such as cross linking with suitable cross-linking agents including silanes, peroxides, radiation of various types, etc. The blend suitability for use in the present invention is determined in the state in which it will be used, eg. post foaming, cross-linking, etc.
- **Bulk polymer:** The polymer(s) that form the continuous phase of polymer blends. Bulk polymers usually constitute the major weight percentage of a polymer blend.
- **Continuous phase:** the phase in a blend that, for the most part at least, constitutes the phase in which the disperse phase is distributed. Included in this definition are co-continuous blend morphologies.
- **Discontinuous phase:** the phase in a blend that is dispersed within a continuous phase.
- **ESCR test:** ESCR test ASTM D1693
- **ESCR:** The ESCR of a polymer blend when tested according to the ESCR test.
- **Ethylene/ α -olefin:** a co- or terpolymer of ethylene with one-or-more α -olefins and optionally incorporating one-or-more polyenes.
- **MFI:** The MFI of a polymer or polymer blend as measured by ASTM D1238 @190°C, 2.19kg. Polypropylene MFIs are usually measured by ASTM D1238 @230°C, 2.16kg
- **mPE:** a polyethylene or polyethylene/ α -olefin copolymer made with a metallocene catalyst and usually having a density between 0.85 and 0.97.
- **Miscible polymer:** a polymer that, when compounded with an ALOP or ALOCA, does not form a separate and distinct phase within the ALOP or ALOCA, i.e. it is essentially miscible with the ALOP or ALOCA.
- **Nanocomposite:** a blend incorporating one-or-more ACAs or ALOCAs that are characterised by having an average particle size $<200\text{nm}$, preferably $<100\text{nm}$. Preferred nano-particles, particularly for blends with improved

barrier properties, are exfoliated clays or organo-clays. This definition of nanocomposite also encompasses masterbatches of nano-particles that have been compounded—and preferably exfoliated—with polymers or other chemicals capable of compatibilising the nano-particles with the bulk polymer of a blend. Preferably the nano-particle are one or more organo-clay.

- **Polyene:** Polyene comonomers suitable for the copolymerisation with other monomers, preferably ethylene, propylene or butene to preferably form ethylene, propylene or butene copolymers suitable for mouldings of the present invention. Suitable polyenes have, in the main, about 3 to 20 carbon atoms, preferably in the range of about 4 to about 20 carbon atoms, most preferably in the range of about 4 to about 15 carbon atoms. In one embodiment the polyene is a diene that has in the range of about 3 to about 20 carbon atoms. Preferably the diene is a non-conjugated diene. Polyenes may be straight chained, branched chained or cyclic hydrocarbon polyenes. The '255 patent contains a number of examples of polyenes suitable for use in tube polymers.
- **Propylene/ α -olefin:** a co- or terpolymer of propylene with one-or-more α -olefins and optionally incorporating one-or-more polyenes.
- **Relatively high MFI:** The MFI of a blend polymer that is greater than the MFI of one or more polymers in the blend. For example, a 1MFI LDPE in a blend containing a 0.5 MFI mPE may be regarded as being a 'relatively high MFI' polymer.
- **Relatively low MFI:** The MFI of a blend polymer that is lower than the MFI of one or more other blend polymers. For example, a 30 MFI mPE in a blend containing a 60 MFI LDPE may be regarded as a 'relatively low MFI' polymer.
- **α -olefin:** α -olefins suitable for copolymerisation with other monomers, particularly ethylene, propylene or butene, to produce ethylene, propylene or butene α -olefins suitable for the production of mouldings of the present invention. These include α -olefins in the range of about 2 to about 20 carbon atoms, preferably in the range of about 3-16 carbons, most preferably in the range of about 2-8 carbon atoms. α -olefins may be saturated or unsaturated straight chained, branched chained or cyclic hydrocarbons, optionally containing functional groups. The '255 patent contains many examples of α -olefins suitable for use in tube polymers.

SPECIFICATION

The present invention relates to blends, particularly polyolefin blends, with improved ESCR, barrier and of other mechanical properties. These improved blends may have a wide variety of MFIs (>0.04 to >100 as measured by I_2) and may be processed by a number of processing methods such as, but not limited to, injection moulding, blow moulding, thermoforming, extrusion, thermoforming and rotomoulding. Blends of the present invention are suitable for a wide variety of different products in which improved ESCR, stiffness, barrier and other physical properties are advantageous. The blends of the present invention are particularly suitable for the production of hollow articles and pressure pipes, wire and cable coatings as well as articles for the automotive, packaging and other industries.

One aspect of blends of the present invention consists of an ALOP and an ALOCA, preferably an ALOP and a nanocomposite, more preferably an ALOP, an ALOCA and a nanocomposite, yet more preferably a polyolefin ALOP, an ALOCA and a nanocomposite, further preferably an mPE ALOP, a polypropylene ALOCA and a nanoclay nanocomposite and most preferably an mPE ALOP together with a LD, MD or HDPE ALOP, a polypropylene homo or copolymer ALOCA and a nanoclay nanocomposite. Note that for the purposes of this application, the term LDPE includes LLDPE.

Higher requirements are constantly being placed upon the mechanical load-bearing capability of polyolefin, and particularly polyethylene, moldings. In particular, there is a requirement for highly environmental-stress-cracking-resistant, impact-resistant and generally stiff, relatively stiff and rigid products which are particularly suitable for the production of automotive mouldings, hollow articles, pressure pipes, wire and cable coatings, etc. The requirement for simultaneous good environmental-stress-cracking resistance and stiffness is not easy to meet, since these are usually regarded as contradictory properties. While stiffness increases with the density of the polyolefin, and particularly polyethylene, environmental-stress-cracking resistance decreases as density increases.

For hollow articles and pressure pipes it has proven advantageous to use blends made from a high-molecular-weight, low-density ethylene copolymer and a low-molecular-weight, high-density ethylene homopolymer, described, for example, by L. L. Bohm et al., Adv. Mater. 4, (1992), 234-238. Similar polyethylene blends are disclosed in EP-A 100 843, EP-A 533 154, EP-A 533 155, EP-A 533 156, EP-A 533 160 and U.S. Pat. No. 5,350,807.

An important application for bimodal polyethylene blends is the production of pressure pipes for conveying gas, drinking water and waste water. Pressure pipes made from polyethylene are increasingly replacing metal pipes. An important factor in applications of this type is very long service life of the pipe, without fear of aging or brittle failure. Even small defects or indentations in a pressure pipe can grow, even at low pressures, and cause brittle failure. This process can be accelerated by temperature increase and/or aggressive chemicals.

It is an object of the present invention to provide a polyolefin, and particularly polyethylene blends, with improved quality of blending and suitable for producing products such as are mentioned above. Another object of the invention was to provide a cost-effective and flexible process for preparation of a blend of this type under mild conditions.

During our work on nanocomposites—and particularly those based on polyolefin ALOPs—we have been struck by the dramatic improvement in ESCR performance that the incorporation of nanocomposites confers on blends. In particular, LD, MD and HD blends that we know from experience have very high failure rates within a couple of hours of the commencement of the test passed it with very low to 0% failure when nanocomposite was incorporated. We believe that nanocomposite blends offering these significant ESCR improvements have utility in applications and manufacturing methods including injection moulding, blow moulding, rotomoulding and extrusion. As an example, the ESCR and other physical property improvements that we achieved with HDPE-based nanocomposite blends confirm that the blends of the present invention have application in pipe, wire, cable and other extrusion applications, injection mouldings for the auto industry amongst others, rigid packaging of various types, film, rotomoulded articles such as drums and tanks, etc.

Blends of the present invention provide improved ESCR and other physical properties than prior art blends. As a consequence they enable the formulation of blends with equivalent ESCR and other physical properties compared to the prior art blends but with higher MFIs that would otherwise be the case, with commensurate improvements in ease of processing savings and consequent savings in power usage and machinery wear-and-tear. The blend physical property improvements also potentially enable moulding weight reduction and down-gauging of films as well as reduced moulding/film weight while achieving a required flex modulus. At the same time they also provide better barrier (eg. impermeability) properties to the mouldings.

A wide variety of polymers may be used as the bulk polymer of a blend of the present invention. These polymers include olefin homopolymers and copolymers, preferably ethylene or polypropylene homopolymers and copolymers with C_3 - C_{20} alpha or beta olefins and/or polyenes, preferably C_3 - C_8 alpha or beta olefins, such polymers having densities ranging from very low to high density (density ranges between 0.85 and 0.97 g/cm³). Also suitable for use in the present invention are ethylene, propylene and butene copolymers with terminal vinyl groups and ethylene, propylene and butene copolymers containing greater than 50% ethylene, propylene or butene which are copolymerised with comonomers such as methyl acrylates, ethyl acrylates, acrylic acid and methacrylic acid, ionomers, and styrene-ethylene/butene-styrene ABA copolymers. These polymers may be made by a wide variety of methods including high and low pressure processes, using a wide variety of catalysts such as Ziegler-Natta and metallocenes, and have molecular structures ranging from linear to highly branched, thus included are LDPE, MDPE and HDPE. Particularly suitable for use in the present invention are plastomers, 'substantially linear' and branched polyethylenes or polypropylenes, copolymers of propylene and ethylene or one or more alpha-olefins, terpolymers of ethylene, propylene and one or more alpha-olefin (of which Montell's Catalloy polymers are an example) and polymers and copolymers of propylene manufactured using metallocene catalysts. Other polymers suitable for use in the present invention include polylactic acid polymers.

US 5451450, the disclosures of which are herein incorporated by reference, describes plastomers as ethylene alpha-olefin copolymers (including ethylene/alpha-olefin/polyene copolymers) with a molecular weight distribution in a ratio M_w/M_n range of 1.5-30, preferably in the range of 1.8-10 and more preferably in the range 2-4. Generally, plastomer polymers comprise ethylene homopolymers and interpolymers of ethylene, with at least one C_3 - C_{20} α -olefin copolymer being especially preferred. The term "interpolymer" is used herein to indicate a copolymer or a terpolymer or the like. That is, at least one other comonomer is copolymerised

with ethylene to make the interpolymers. Generally, the α -olefins suitable for copolymerisation with ethylene to form plastomers contain in the range of about 2 to about 20 carbon atoms, preferably in the range of about 3-16 carbons, most preferably in the range of about 3-8 carbon atoms. Illustrative non-limiting examples of such α -olefins are propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, and 1-dodecene and the like. Polyene comonomers suitable for the copolymerisation with ethylene to form plastomers suitable for the present invention have, in the main, about 3 to 20 carbon atoms, preferably in the range of about 4 to about 20 carbon atoms, most preferably in the range of about 4 to about 15 carbon atoms. In one embodiment the polyene is a diene that has in the range of about 3 to about 20 carbon atoms, and may be a straight chained, branched chained or cyclic hydrocarbon diene. Preferably the diene is a non-conjugated diene. Non-limiting examples of ethylene/ α -olefin plastomers suitable for the present invention include ethylene/butene-1, ethylene/hexene-1, ethylene/octene-1 and ethylene/propylene copolymers. Non-limiting examples of terpolymer plastomers suitable for the present invention include ethylene/propylene/1,4 hexadiene and ethylene/octene-1/1,4-hexadiene.

Plastomers and 'substantially linear polyethylenes' are produced mainly with the use of metallocene catalysts. US 5281679, the disclosures of which are herein incorporated by reference, shows a method of producing metallocene homo and copolymers with a broad molecular weight distribution, generally in the range of 3-30, which have improved tensile and impact strength relative to Ziegler-type catalysed polymers. They are also characterised by having considerably narrower short chain branching distributions, and lower hexane extractables. Such polymers are suitable for use in the present invention.

We have found that plastomers, 'substantially linear polyethylenes', metallocene branched polyethylene copolymers, propylene α -olefin interpolymers and metallocene propylene polymers and interpolymers are preferred for use in the present invention for the production of mouldings of the present invention. A key characteristic of plastomers, 'substantially linear polyethylenes', metallocene branched polyethylene copolymers, propylene α -olefin interpolymers and metallocene propylene polymers and interpolymers is their composition distribution ie. the uniformity of distribution of comonomer within and among the molecules of the polymer. Plastomers, 'substantially linear polyethylenes', metallocene branched polyethylene copolymers, propylene α -olefin interpolymers and metallocene propylene polymers and interpolymers are generally made using metallocene catalysts, which are known to incorporate comonomer very evenly among and along the polymer molecules they produce. Thus most molecules of a particular plastomer, 'substantially linear polyethylenes', metallocene branched polyethylene copolymers, propylene α -olefin interpolymers and metallocene propylene polymers and interpolymers will have roughly the same comonomer content, and within each molecule the comonomer will be super-randomly distributed. Ziegler-Natta catalysts generally yield copolymers having a considerably broader composition distribution - specifically the comonomer distribution in polymers thus produced will vary widely among the polymer molecules, and will also be less randomly distributed within a given molecule.

In terms of densities, the plastomers preferred for use in the process of the present invention are comparable to VLDPE or ULDPE, which are also copolymers of ethylene with α -olefins, such as butene, hexene or octene. They are generally defined as ethylene α -olefin copolymers with densities between 0.850 and about 0.915.

The process for making VLDPEs is generally described in EP 120503. Plastomers, even those with the same density as VLDPEs, have greatly different physical properties due to differences in the manufacturing process - primarily in the use of metallocene catalysts. In general, a VLDPE compared to a plastomer of similar density has a significantly higher melting point and softening point, molecular weight/size distribution higher than 3 and a higher level of crystallinity.

Elastic substantially linear olefin polymers as disclosed in a number of patents including US 5,272,236 US 5,278,272, US 5,380,810, US 5,525,695 and US 5,665,800 all of which are incorporated herein by reference. As an example of an elastic substantially linear olefin polymer, US Patent 5,578,272 describes one type as having a critical shear rate at onset of surface melt fracture of at least 50% greater than the critical shear rate at onset of surface melt fracture of an olefin polymer having the same I_2 and M_w/M_n . These polymers also have a processing index (PI) less than or equal to a comparative linear olefin polymer at the same I_2 and M_w/M_n . Elastic substantially linear polymers comprising ethylene homopolymers and interpolymers of ethylene with at least one $C_3 - C_{20}$ α -olefin copolymers are especially preferred. The term "interpolymer" is used herein to indicate a copolymer or a ter polymer or the like. That is, at least one other comonomer is copolymerised with ethylene to make the interpolymer.

The term 'substantially linear' polymers means that the polymer backbone is substituted with about 0.01 to about 3 long chain branches per 1000 carbons, most preferably 0.03 to 1 long chain branches per 1000 carbons. The term "linear olefin polymer" means that the polymer does not have long-chain branches, as for example the traditional linear low density polyethylene or linear high density polyethylene polymers made using Ziegler polymerisation processes (eg US Pat 4076698 and 3645992), the disclosures of which are incorporated herein by reference.

The SCBDI (short chain branch distribution index) is defined as the weight percent of molecules having a comonomer content within 15% of the median total molar comonomer content. The SCBDI of the substantially linear polymers suitable for the present invention is preferably greater than about 30%, and especially greater than about 50%.

A unique characteristic of the substantially linear polymers of the present invention is a highly unexpected flow property where the I_{10}/I_2 value is essentially independent of polydispersity index (ie. M_w/M_n). This is contrasted with conventional polyethylene resins having rheological properties such as the polydispersity index, the I_{10}/I_2 , increases. The density of the ethylene or ethylene/ α -olefin substantially linear olefin polymers in the present invention is generally from about 0.85g/cm^3 to about 0.97g/cm^3 , preferably from about 0.85 to 0.92g/cm^3 .

The substantially linear polymers preferred for use in the process of the present invention have processability substantially similar to that of high pressure LDPE, while possessing the strength and other physical properties similar to those of conventional LLDPE without the benefit of special adhesion promoters (eg processing additives such as Viton fluoroelastomers made by Du Pont).

US Patent 5,525,695 (the disclosures of which are herein incorporated by reference) describes a manufacturing method for 'substantially linear polyethylenes', and characterises them as having:

- A. a density from about 0.85 g/cm^3 to about 0.97 g/cm^3 ;
- B. an MI from 0.01 g/10 min to 1000 g/10 min ;
- C. and preferably a melt flow ratio of I_{10}/I_2 from about 7 to 20; and
- D. a molecular weight distribution M_w/M_n preferably less than 5, especially less than 3.5 and most preferably from about 1.5 to 2.5.

Elastic substantially linear olefin polymers can be made with broader molecular weight distributions by means of the appropriate selection of catalysts for the polymerisation process as described in US 5,278,272. Broader MWD material exhibits a higher shear rate or shear stress dependency. In other words, generally the broader the MWD, the higher the effective MFI at high shear, and hence the better the processing characteristics. Broad molecular weight 'substantially linear olefin polymers', plastomers and metallocene branched polyethylenes are particularly suited to the production of mouldings of the present invention by the process of the present invention.

It has been established that polymers, but particularly plastomers and substantially linear olefins, having higher-than-normal I_{10}/I_2 values which are essentially independent of polydispersity index (ie. M_w/M_n) and metallocene polypropylene homo and copolymers are particularly suited to the manufacture of mouldings of the present invention having good ESCR and other physical/chemical properties. As discussed in US 5,281,679 the disclosures of which are incorporated herein by reference, broadening the molecular weight distribution of a polymer - and particularly polyethylene and its copolymers - increases the tensile strength and impact strength of products made therefrom. The main reason for high I_{10}/I_2 in a polymer is the presence of both high MW and low MW molecules in the polymer. It is believed that the high MW molecular fraction contribute significantly to improving the ESCR properties of the polymer, while the low MW molecular fraction contribute to the improved processability of the polymer by increasing the shear sensitivity of the polymer, thereby enabling the polymer to be molded into mouldings of the present invention in spite of the apparently low MFI (usually measured as I_2) of the polymer.

High I_{10}/I_2 polymers suitable for the present invention may be produced by a variety of methods. These include:

- 1) intimately blending two or more polymers having different molecular weights in appropriate blending equipment;
- 2) producing bi or multi modal polymers with high I_{10}/I_2 by means of 'tandem' reactors; and
- 3) producing bi or multi modal polymers with high I_{10}/I_2 in a single reactor using appropriate catalysts.

The catalysts used to produce bi or multi modal polymers with high I_{10}/I_2 may be selected to produce:

- 1) broad molecular weight distribution polymers (eg. with molecular weight distribution in the 3-30 range as described in US patent 5,281,679 which is incorporated herein by reference); or
- 2) effectively two or more polymers, each having either a narrow or broad molecular weight distribution as desired. US 5,539,076 the disclosures of which are herein incorporated by reference, describes a method of manufacturing bi or multi

modal polyethylene polymers with densities between 0.89 and 0.97 in a single reactor.

Experimentation has shown that a single component of a blend, preferably a polyolefin component, more preferably a polyethylene component, may advantageously be substituted with a blend of 2 or more polymers of the same polymer type to achieve a density similar to that of the single substituted component. The effect of this substitution will often result in the reduction of the crystallization half-time and mould cycle time of polymer blends. While not wishing to be bound to any theory, we believe the higher density polyethylene nucleates the lower density polyethylene accelerating the rate of crystallization. Since the blend freezes faster and at a higher temperature than a similar density single polymer, the moulded article can be removed or ejected from the mould sooner, resulting in a shorter overall moulding cycle time. Also, the modified crystal morphology of the moulded blend provides improved physical properties (i.e. total impact energy, ESCR, etc.) compared to a moulded similar density single polymer.

We have found that bimodal polyethylene blends, for example and including blends made from a high-molecular-weight ethylene copolymer and a low-molecular-weight ethylene homo- or copolymer and having a density of from 0.93 to 0.97 g/cm³, have improved ESCRs and processing parameters relative to single components with the same density and MFI as the bimodal blend, and that such bimodal blends have utility in as a component of blends of the present invention. These bimodal blends preferably comprise from 40 to 60% by weight of the high-molecular-weight and from 60 to 40% by weight of the low-molecular-weight component.

We have found that blend ESCR decreases with increasing MFI of the LD/MD/HDPE components in the blend, particularly when LD/MD/HDPE is an ALOP of a blend of the present invention. This is no doubt due to the well-established direct relationship between ESCR and polymer—particularly polyethylene polymer—MW and the fact that the LD/MD/HDPE contributes very few tie molecules to the blend. This means that in order to counteract the negative ESCR effects of high MFI LDPEs and similar polymers in a blend, it is necessary to add increasing amounts of ALOCAs and/or to increase the copolymer % in the mPE component, i.e. to decrease the density of the mPE used and/or to increase the amount of mPE in the blend, and/or to increase the % of nanoparticles in the present invention.

Other polymers suitable for mouldings of the present invention are silane-grafted or copolymerised polymers. Such polymers can be crosslinked post-processing, resulting in mouldable/processable, crosslinked polymer compounds which provide the ease of processability and design/process flexibility of relatively low viscosity polymers while achieving the strength and other benefits of higher viscosity, cross-linked polymers and copolymers. These polymers also eliminate the need for prolonged cycle times and elevated temperatures to achieve in-mould crosslinking. There are numerous patents describing various aspects of the method of preparing and crosslinking of various silane-based compositions that can be used in the present invention. Included are US Patents, 5,055,249, 4,117,063, 4,117,195, 4,413,066, 4,975,488 and 3,646,155, the disclosures of which are incorporated by reference. Polymers suitable for use in the nanocomposites of the present invention are exemplified, but not limited to, polymers such as polyolefins, including plastomers, substantially linear metallocene polyethylene α -olefin copolymers, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), isotactic, syndiotactic and

atactic polypropylene (PP) such as polypropylene with varying degrees of isotacticity such as are described in, amongst others, WO 01/27169, WO 99/52955, WO 99/52950 and WO 99/29749, α -olefin copolymers of ethylene, propylene or butene, preferably α -olefin copolymers of ethylene, propylene or butene prepared using metallocene or similar catalysts capable of producing super-random distribution of the α -olefin copolymer within and amongst the molecular chains, polyamides such as poly(m-xylenedipamide) (MXD6), poly(hexamethylenedipamide) and poly(ϵ -caprolactam), polyesters such as poly(ethylene terephthalate), polycarbonates and polyacrylonitriles.

The ALOCA is preferably a polymer and when blended with the ALOP results in blends having properties which, when blended is used to mould mouldings of the present invention, are superior to the original constituents or the neat polymers. The ALOCA may be selected from the group consisting of ethylene vinyl acetate; ethylene vinyl alcohol; plasticised polyvinyl acetate and polyvinyl alcohol; alkyl carboxyl substituted polyolefins; copolymers of anhydrides of organic acids; epoxy group containing copolymers; chlorinated polyethylene; ethylene-propylene-butylene etc. copolymers; ultra low density, very low density, low density, medium density and high density polyethylene; polypropylene, polybutylene and copolymers thereof; polyester ethers; polyether-esters (such as DuPont's Hytrel range); acrylonitrile-methacrylate copolymers; block copolymers having styrene end blocks; half esters; amino and alkoxysilane grafted polyethylenes; vinyl addition polymers; styrene-butadiene block copolymers; acid grafted polyolefins; vinyl pyrrolidine grafted polyolefins; block copolymers of dihydric monomers; propylene graft unsaturated esters; modified polyolefins comprising amide, epoxy, hydroxy or $C_2 - C_6$ acyloxy functional groups other polymeric compatibilisers suitable for use with polyolefins; particles coated with any of the above; and mixtures thereof. In the above ALOCAs the functional groups are generally incorporated into the modified polyolefin as part of an unsaturated monomer which is either copolymerised with an olefin monomer or grafted onto a polyolefin to form the modified polyolefin.

Alkyl carboxyl substituted polyolefins may include substituted polyolefins where the carboxyl groups are derived from acids, esters, anhydrides and salts thereof. Carboxylic salts include neutralised carboxylic acids and are often referred to as ionomers (eg. Surlyn). Typically acids, anhydrides and esters include methacrylic acid, acrylic acid, ethacrylic acid, glycidyl maleate, 2-hydroxyacrylate, diethyl maleate, maleic anhydride, maleic acid, esters of dicarboxylic acids, etc. Preferred examples include ethylenically unsaturated carboxylic acid copolymers such as polyethylene methacrylic acid and polyethylene acrylic acid and salts thereof.

Copolymers of anhydrides of organic acids include copolymers of maleic anhydride as well as copolymers of cyclic anhydrides.

Poly-2-oxazoline compounds and fluoroelastomers are also suited for use as ALOCAs. Incorporation of 1-40%, most preferably 2-20% of poly-2-oxazoline compounds is preferred. These ALOCAs improve the adhesion of the PE blend to various substrates, which may make them useful for printing or labelling. The compatibilizing agent comprises an α -olefin copolymer substrate grafted with amounts of monovinylidene aromatic polymer. Preferably, the α -olefin copolymer substrate is a terpolymer of ethylene, propylene and a non-conjugated diolefin.

An ALOCA or ALOHMFCA is usually a polymer that is compatible, but not miscible, with an ALOP in a blend. Preferred ALOCAs and ALOHMFCAs are ethylene, propylene or butene homo or α -olefin interpolymers, preferably produced using a metallocene or similar catalyst. ALOCAs and ALOHMFCAs may also be terpolymers, such as one comprising ethylene, propylene or butene, an additional and different α -olefin to the first α -olefin and a diene, preferably a diene containing 7 to 10 carbon atoms, and having an amount of diene effective to cause an increase in MFI compared to corresponding linear copolymer without diene. Polymers conforming to the above description are described in US 6,509,431, and depending on their MFI and other characteristics, may also be used as ALOPs or ALOCAs.

Because the addition of PP in particular resulted in such a dramatic improvement in the ESCR of mPE blends, particularly relatively high MFI blends, we commissioned analyses from an independent research laboratory to identify the reasons for this unexpected effect. DSC analysis in particular showed that PEs in general, but relatively high MFI mPEs in particular, interact with propylene and many of its copolymers and in doing so the crystallinity of the PE component of the blend is reduced. We believe that this effect is occurring primarily at the PP/PE interface and that the propylene polymer functions as both an interacting filler and crystallising agent for the PE and that in doing so it results in increases in the number of amorphous regions within the PE. We further believe that the combination of the increase in the number of amorphous areas within the blend matrix and the decrease in crystallinity at the PE/PP interfaces act to reduce or disperse the moulded-in stresses in the moulded part, thus increasing its ESCR. As such amorphous areas can help relieve moulded-in stresses within the mouldings, they increase the ESCR of the blend relative to blends with ALOCAs that don't so interact with the ALOP. For example, many homo and copolymers of PP are able to interact with PE ALOPs so as to reduce interface crystallinity, whereas ionomers such as Surlyn 9970 don't appear to have this ability.

There is a wide range of polymers that are suitable for use as ALOCAs in blends of the present invention. In essence, virtually any polymer that is compatible, or can be made compatible via, for example, a compatibiliser, with the ALOP of a blend and which has the effect of increasing the ESCR of the ALOP is suitable for use as an ALOCA in blends of the present invention. To illustrate this, we have successfully used various nylons, polyesters and ionomers as ALOCAs in blends of the present. A number of such formulations showed interesting properties, in some cases including improved barrier properties. For example, we found that a number of blends incorporating nylon 6 as the ALOCA and which had been compatibilised showed improved barrier properties to hydrocarbons such as petrol.

ALOCAs with MFIs up to 100, such as Basell's SC973 polypropylene/ethylene copolymer, have been successfully used in blends of the present invention. Similarly, ALOHMFCAs, particularly PP ALOHMFCAs such as 350 MFI PP homo and copolymers, may be particularly useful in blends of the present invention. The ALOCA usually forms the discontinuous phase, and may be added in sufficient quantity to increase the ESCR of the blend to the required level. In general, the greater the percentage of ALOCA in a blend, the better the ESCR. The suitability of particular blends for particular applications can be established by experimentation. Some of the polymers suitable for use as ALOCAs are described in the relevant sections in the '255 patent.

Because the ALOCA may confer other desirable properties to a moulding in addition

to improving the ESCR of a moulding, it may also be added in quantities in excess of those required simply to achieve the desired ESCR. Again, the level of ALOCA required to achieve a particular property(s) for a moulding may be determined by experimentation.

The ALOCA is advantageously a polypropylene homo and/or copolymer. Suitable polypropylene-based ALOCAs include isotactic, syndiotactic and atactic polypropylene of various MFIs, densities and crystallinities as would produce desired mouldings of the present invention. Particularly when blended with ALOPs containing relatively low molecular weight plastomers and/or substantially linear polyethylenes, a wide variety of polypropylene polymers possessing a very wide range of MFIs, densities and crystallinities will produce blends suitable for use in the manufacture of mouldings of the present invention. The propylene-based ALOCAs may be propylene homopolymers, block or random copolymers with various α -olefin copolymers, preferably copolymers of propylene with ethylene or butene in which the ethylene or butene component constitutes less than 35% of the polymer. Often it is advantageous that the propylene-based ALOCA has a crystallinity that is greater than the overall crystallinity of the ALOP phase of the composition. The propylene-based polymer used as the ALOCA may be manufactured using a variety of catalysts, including metallocene catalysts.

Preferably, but by no means essentially, the propylene based polymer will have a MWD of from 1.8 to 4.0 and a narrow composition distribution that is characteristic of metallocene or similar catalysed propylene polymers. However, propylene based polymers such as are cited in US 6,476,173 and which have MWDs up to 20 will often produce good results. Random ethylene/propylene/vinyl aromatic interpolymers such as ethylene/propylene/styrene interpolymers may also be used as the ALOCA in the present invention.

In general, it has been established that the higher the flexural modulus of the propylene-based ALOCA, the higher the flexural modulus of a moulding. Therefore if a more flexible moulding is required, it is advantageous to use a propylene-based polymer that has a lower flexural modulus. This in turn often translates into propylene/ α -olefin copolymers with higher percentages of α -olefin copolymer, i.e. the higher the percentage of α -olefin copolymer, the lower the flexural modulus of the composition. The flexural modulus of the ALOCA may be reduced by the addition to it of a polypropylene-compatible low flexural modulus polymer. Examples of such polymers are Basell's Catalloy KS-084P and KS-357P - these products are believed to be terpolymers of propylene, ethylene and butene. Other such copolymers and/or terpolymers may be used.

In general, the ESCR of a particular ALOP/ALOCA blend increases as the percentage of the α -olefin content of the polypropylene-based ALOCA component of the blend increases. Thus for a given percentage of a blend, a propylene/ α -olefin copolymer will usually impart a higher ESCR to a particular ALOP/ALOCA blend than will the same percentage of propylene homopolymer with the same MFI.

In essence, a PP homo or copolymer that is capable of interacting with the ALOPs of blends of the present invention, preferably by means of acting as a nucleating agent, is suitable for inclusion in blends of the present invention as an ALOCA.

We have established that we can incorporate high MFI PPs (eg. Basell's 100 MFI Profax Ultra SG982) into blends without adversely affecting the physical properties of

the resultant mouldings of the present invention. This is important because it enables the use of high-MFI PPs to improve blend ESCR and at the same time to increase the overall MFI of the blend to improve processing characteristics.

Preferred blends of one aspect of the present invention are polymer blends containing nanocomposites and/or relatively high levels of other ACAs capable of nucleating the ALOPs of the blend. Usefully, the nanoparticles in blends of the present invention are clays, most frequently organo-clays. Blends of the present invention are particularly useful for the production of products with significantly improved ESCR and barrier properties relative to the same blend without the nanoparticles. The incorporation of nano-sized particles into blends also has the benefit of improving the ESCR of the blend relative to the same blend without the nano-sized particles, which in turn significantly enlarges the blend formulation window.

Further, we have found that some types of polymers, preferably unsaturated polymers such as polyvinyl chloride and polystyrene, more preferably polyolefins and even more preferably plastomers, 'substantially linear polyethylene', metallocene branched polyethylene and polypropylene copolymers and most preferably plastomers and 'substantially linear polyethylene' polymers and polypropylene copolymers having densities between 0.85 and 0.92 may, with the addition only of nucleating agents as a means of improving the ESCR of the mouldings of the present invention, be used to produce mouldings of the present invention suitable for packaging some less aggressive products. However, the addition of compatible polymers such as polypropylene and polypropylene copolymers to such polymers in addition to the nucleating agents results in better overall ESCR resistance, and are generally preferred.

Assuming that a PP ALOCA in a PE ALOP blend has an average spherical particle diameter of 500nm, each particle has a surface area of $785,000\text{nm}^2$ and a volume of $65,000,000\text{nm}^3$. By comparison, a typical clay platelet has a thickness of $\pm 1\text{nm}$, which means that in order to have the same volume as the 500nm diameter sphere, it must have L X W dimensions equivalent to 8062 X 8062nm. Assuming that the average clay platelet is 200 X 200 X 1nm (i.e. it has an aspect ratio of 200), it has a volume of $40,000\text{nm}^3$. Therefore in volume terms, one 500nm diameter PP spherical particle is equivalent to 1,625 clay platelets. Assuming that the density of the clay is ± 1.8 (i.e. 2X that of the PP), this means that a given weight percentage of exfoliated clay platelets has $\pm 800\text{X}$ as many particles as the PP. In other words, in terms of theoretical nucleation ability the clay-dimension particles offer 800 times as many nucleation sites/particles as the PP. This goes a long way towards explaining the increase in blend ESCR that occurs when nanocomposites are added to the blend or substituted for some of the PP in blends.

The addition of fine, ultra-fine and/or nano-sized particles for the production of mouldings of the present invention frequently leads to improved properties of the blends of the present invention. Such blends may contain fine, ultra-fine or nanoparticle-sized polymers or clays or metal oxides such as ultra-fine barium sulphate (which may have a particle size of 10nm), particles of other inorganic metal oxides such as those of zinc, electrically conductive tin, e.g., antimony containing tin oxide, iron, zirconium, aluminium, chromium, yttrium, europium, mixtures thereof, among others. Fine, ultra-fine and nano-sized particles may be powders having a primary crystallite size of from about 1 to 200 nm, preferably $<100\text{nm}$ and often from about 4 to about 60 nm. These crystallites can form agglomerates with an average size up to about 300 nm. Also included in the definition of nanocomposites are blends

containing non-clay crystallising/nucleating agents capable of crystallising/nucleating the ALOP(s) and/or ALOCA(s) of the blend. Although for 'normal' mouldings commercial nucleating agents are often added in quantities at 0.1% or less, for the present invention it is sometimes preferable to add crystallising/nucleating agents in quantities greater than 0.1 weight percent, preferably >0.3%, more preferably >0.5% and sometimes >1%. The optimum amount added to a particular blend may be determined by experimentation. There are many non-clay crystallising/nucleating agents, such as metal salts of organic acids such as sodium and lithium benzoates, sorbitol derivatives, glycol derivatives, etc. which are useful for the formulation of blends of the present invention and are well known to those skilled in the art.

Nanoparticles, preferably those with very high aspect ratios and particularly, but not exclusively, those consisting of modified clay minerals, can advantageously be used as an ACA for the manufacture of mouldings of the present invention. In addition to enhancing the barrier properties of mouldings, nanoparticles can also enhance their heat stability, flame retardancy and other mechanical properties.

When the nanoparticle is a clay, organo-clay or other particle of nano-proportions with a high aspect ratio, even small weight percentages of the nanoparticles relative to the polymer material provide increases in the ESCR, impermeability and other physical properties of mouldings of the present invention. As a guide, the higher the average aspect ratio of the nanoparticle and the greater its average diameter, the greater the improvement in barrier properties that the particles will confer on the nanocomposite. For example, a nanocomposite in which the nanoparticles have an average aspect ratio of 1000 will usually have better barrier properties than a nanocomposite with the same weight percentage and chemical type of nanoparticles but with an aspect ratio of 100. Conversely, and using the above example, the nanocomposite in which the nanoparticles have an average aspect ratio of 100 will often have a better ESCR than the nanocomposite with the 1000 aspect ratio nanoparticles because there will be a greater number of individual particles in the former nanocomposite, which in turn will result in a greater number of nucleation sites for the polymers, hence a greater number of polymer crystals will be formed, which in turn will result in an inherently better ESCR. When the nanoparticle is a particle that does not have a specially high aspect ratio, such as nano-sized TiO_2 , other metal oxides, etc., even small weight percentages of the nanoparticles relative to the polymer material provide increases in the ESCR and other physical properties of mouldings of the present invention, but the barrier properties of such nanocomposites will generally not be as good as a nanocomposite in which the nanoparticle has a high aspect ratio. Typical non-fine TiO_2 such as are extensively used in the plastics industry, such as Dupont TiO_2 grades for plastic applications, have a mean particle size of 350nm (Grade R960) and 220nm (Grade R104), and so do not fall within the scope of this invention.

Nanoparticle/polymer blends for mouldings of the present invention may be fabricated through various methods. One such method is compounding wherein the ingredients are intimately melt-mixed together into as nearly a homogeneous mass as is possible. Other methods of integrating the polymer layer in between the clay/organo-clay platelet include in situ polymerisation, solution intercalation and melt exfoliation. The organo-clays preferred for tube production differ from ordinary untreated clays in the fact that the untreated clays typically form only ordinary phase-separated mixtures when blended or mixed with a polymer. The clays which are organically modified are more easily dispersed in the polymer matrix and can form a nanocomposite of two types: i.e. mainly intercalated or mainly exfoliated structures.

In order to obtain better compatibility between the polymer—and particularly polyolefin polymers—and the organo-clay it is often desirable that the organo-clay contains substituted alkyl side chains. Blends particularly suitable for mouldings of the present invention comprise between about 0.01 and about 25 wt %, preferably between 0.5 and 25 wt %, more preferably between 0.5 and 15 wt % and most preferably between 0.5 and 10 wt % of at least one expanded organo-clay

The organo-clays suitable for tube production generally have a particle size from about 1 to about 10,000 nanometres, desirably from about 100 to about 2,000 nanometres, and preferably from about 200 to about 500 or 1,000 nanometres. When the main polymer to be used to form the nanocomposite and/or nanocomposite master-batch (i.e. a concentrate for subsequent dispersion in another polymer) is a polyolefin, it has been found that, all other things being equal, the greater the degree of short-chain branching in the polymer (as measured by SCBI) the greater the extent of exfoliation of the organo-clay, and hence the better the overall properties of the nanocomposite. All things being equal, in the case of olefin/ α -olefin and other copolymers the greater the percentage of α -olefin or other copolymer in the polymer the greater the extent of exfoliation of the nanocomposite. Also, polymers exhibiting super-random distribution of the monomers within the polymer molecules are particularly suited to the production of nanocomposites of the present invention as their use tends to result in greater degrees of exfoliation than similar polymers not exhibiting super-random distribution of the monomers. Such super-random polymers may be catalysed by metallocene or similar catalysts which are well known in the art.

Particularly advantageous are blends in which the fine, ultra-fine or nanoparticle-sized particles have the following characteristics:

- 1) Average particle size between 0.9 and 100nm and an aspect ratio of between 10 and 2000.
- 2) Preferably has a thickness of <2nm and a diameter between 10 and 1000nm.

Typically, clays of various types such as the following are preferred ACAs which may have the above characteristics. Preferred swellable layered clay materials are phyllosilicates of the 2:1 type having a cation exchange capacity of 50 to 200 milliequivalents per 100 grams of mineral. The most preferred swellable layered clay materials are smectite clay minerals such as montmorillonite. Other non-clay materials having the above described ion exchange capacity and size, such as chalcogens may also be used as the source of platelet particles for polymer blends for tube production.

Much of our formulation work has been directed at maximising properties such as toughness, modulus, impact strength and ESCR without sacrificing processability through the use of blend compositions comprising two or more polymer components of differing molecular structures. In the case of many PE-ALOP-based blends of the present invention we have used mPEs with relatively high comonomer content for tie molecule content in conjunction with LLD, LD, MD and HDPEs for processability. The mPE may have a relatively high or relatively low MW compared to the LLD/LD/MD/HDPE, depending on the application and the desired physical properties of the moulding.

Blends consisting of a relatively high molecular weight (i.e. relatively low MFI) copolymer in combination with a relatively low molecular weight (i.e. relatively high MFI) homopolymer or copolymer with higher crystallinity than the relatively high molecular weight polymer have been found to possess acceptably good processability

and low temperature mechanical properties. This is particularly the case for blends with an MFI >1, more preferably >10, yet more preferably >30 and most preferably >50. While not wishing to be bound by any theory, it is believed that the relatively low MFI copolymers, preferably copolymers characterised by super-random distribution of comonomers within the polymer chains, produce a high number of 'tie' molecules within the blend which in turn counteract the inherently poor ESCR of the relatively low MW/higher crystallinity homo or copolymer component(s). This combination of polymer types results in blends with improved processability yet acceptable ESCR and other physical and chemical properties.

The relatively high MFI component(s) of such blends are preferably homo or copolymers with a lower copolymer content than the relatively low MFI component(s), may be polyethylene highly branched or linear homo and copolymers such as are produced by various polymerisation processes, including free radical polymerisation, Z-N catalysed processes or particular processes using metallocene or similar catalysts. When the relatively high MFI component(s) are polyethylenes, they may be ultra-low, low, medium and/or high density polyethylene homo or copolymers.

It is believed that the relatively high MFI component(s) provide the blend with improved processing characteristics relative to the relatively low MFI component, and in addition improve the cycle time of the moulding process by accelerating the crystallisation of the relatively low MFI blend component by acting as nucleating agents. Also, because the relatively high MFI component(s) usually has a higher crystallinity than the relatively low MFI component, they usually make removal of the moulding from the tool easier than would otherwise be the case if the relatively low MFI component(s) alone comprised the blend. An additional advantage of the relatively high MFI component(s) is that it raises the MFI of the blend, thereby lowering the processing pressure and energy expenditure necessary to process the polymer.

To summarise our findings with regard to the relative characteristics of the mPE and higher crystallinity PE components on mPE/"higher-crystallinity PE"/PP blends, we have found that preferred blends consist of a relatively low MFI mPE copolymer in combination with a relatively high MFI "higher crystallinity PE" homopolymer or copolymer that has a higher crystallinity than the mPE component. Such blends have surprisingly good processability and physical properties as well as lower costs than mPE/PP blends and provided that they have an ESCR sufficiently good for the intended application, are particularly useful blends of the present invention.

In blends of the present invention the ALOCA is used in an amount at least sufficient to improve the environmental stress crack resistance of the blend. In certain formulations, 2% or less of an ALOCA is sufficient to improve the environmental stress crack resistance of the polymer blend relative to the environmental stress crack resistance of the plastomer.

The ALOCA may also be used in amounts in excess of those required to compatibilise the polymer blend in order to improve the physical characteristics of said polymer blend so as to optimise the moulding characteristics of said polymer blend and/or general properties of the moulded product such as stiffness. Typically, the ALOCA is used in an amount of from about 2 to about 98 weight percent of the polymer blend, although lower amounts may be used in certain polymer blends. The optimum amount for a specific formulation will depend on the properties required and can be

determined by experimentation. Further it has been found that inclusion of percentages of ALOCAs that are greater than necessary for increasing the environmental stress crack resistance of the polymer blend will often also enable the improvement of the polymer blend properties such as tear and impact strength, barrier properties, chemical resistance, processing and product feel. For example, the incorporation of greater than necessary percentages of polypropylene to improve the environmental stress crack resistance of a polyethylene blend to the desired level may improve the chemical resistance and reduce the water vapour and water transmission ratio of the polymer blend compared to polymer blends containing the minimum amount of polypropylene required to improve the environmental stress crack resistance only. Further, it has been found that the inclusion of greater-than-necessary percentages of compatible agent may enable the incorporation of greater percentages of other polymers than would otherwise be consistent with this invention. Thus, using the ALOCA in such quantities may enable the incorporation of greater-than-otherwise-possible amounts of such beneficial, essentially incompatible other polymers such as nylons and EVOH - with concomitant improvements in properties such as tear and impact strength, barrier properties, chemical resistance and/or product feel.

Barrier resins may be incorporated into the polymer blends of the present invention. Barrier resins that may be compatibilised with the at least one polymer include: condensation polymers such as polyamides, polycarbonates and various esters such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyethylene naphthalate (PEN); polyvinylchloride (PVC); polyvinylidene chloride (PVDC); ethylene vinyl alcohol (EVOH); polyvinyl alcohol (PVOH); ethylene vinyl acetate (EVA); EMA, EMAA, EEA; ionomers; monovinylidene aromatic polymers and copolymers; ethylene, propylene and butylene copolymers; chlorosulfated polyethylene, polyisoprene and polychloroprene, polyalkalenephylene ester and ester ether; phenylformaldehyde; polyacrylate; polyester ethers; acrylonitrile-methacrylate copolymers; nitrile copolymers; polyacrylonitrile; polyurethane and polyacetyls. It will be appreciated that certain barrier polymers will be more or less compatible with the at least one polymer than others. For example, EVOH with a sufficiently high ethylene content will be compatible with the at least one polymer, particularly when said polymer is an ethylene copolymer such as a plastomer, while EVOH with a relatively low ethylene content will be essentially incompatible. Barrier properties of the polymer blends of the present invention may be further enhanced by the addition of additives capable of reacting with or absorbing deleterious chemicals such as oxygen and other gases.

Clays naturally tend to exist as 'tactoids' or 'galleries', which are an agglomeration of up to and sometimes greater than 100 individual clay platelets. In order to achieve the maximum benefit from the nanocomposites, and particularly clay nanocomposites, the individual nanoparticles need to be evenly dispersed throughout the polymer matrix. In the case of clays, the process of separating the individual clay platelets is called exfoliation. Exfoliation may be achieved in a number of ways, but the most commonly used method is to introduce an appropriate intercalant into the galleries of the clay and then apply shear to separate the individual platelets. The intercalant also should preferably have a functional group that can interact with the polymer and effectively link the platelets to the polymer. An epoxy resin such as bisphenol A can be used as an intercalant.

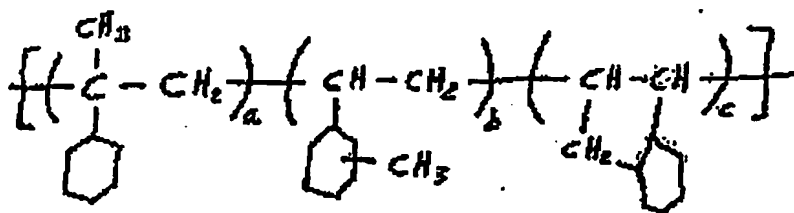
There are a number of intercalants suitable for the production of nanocomposites for the present invention. Particularly useful for polyolefin-ALOP blends are intercalants

comprising an organic compound having a non-polar portion bonded to a polar portion. The non-polar portion may, for example, be a saturated oligomer of isoprene which tends to be compatible with non-polar polymers, especially copolymers of both propylene and ethylene. The polar portion tends to have an affinity for the silicate platelets of the clay material. Consequently, the organic compound enhances the compatibility of the intercalated clay materials that, when melt blending with sufficient shear to exfoliate the intercalated clay material, results in the exfoliation of intercalated clay into the polymer.

There are a number of ways in which nanocomposites can be prepared and which are described in the literature. Some of the methods that may be particularly suited to the production of nanocomposites suitable for tube production are highlighted below. Of particular interest for the production of mouldings of the present invention are nanocomposites in which the bulk polymer is a polyolefin such as polyethylene or polypropylene or a polyester such as PET or PEN, said polymers being particularly suited, by reason of cost and other polymer properties, for the production of mouldings of the present invention. As is well known, forming nanocomposites with polyolefins presents special challenges due to the essentially non-polar nature of said polymers and the consequent difficulties in achieving significant degrees of exfoliation of the organo-clay. However, the development of new intercalants and methods of achieving such nanocomposites have resulted in improvements in the performance and manufacture of polyolefin-clay nanocomposites. These developments, together with the exceptionally high shear rates generated during the injection moulded tube process, and which facilitate the exfoliation of non-exfoliated clays, can produce polyolefin nanocomposites that have good barrier and other beneficial properties.

A preferred way of improving the degree of exfoliation of organo-clays in polyolefins is through the addition and compounding together of a modified polyolefin—such as a maleic anhydride modified polyolefin polymer or oligomer—and an organic cation (such as a quaternary ammonium) exchanged multi-layered clay. This process results in a masterbatch which is then added to and compounded with a suitable polyolefin. The organo-clay thus produced has sufficient polarity to enable significant exfoliation of the clay when subjected to the shear stress during compounding with the polyolefin, and particularly during the high shear manufacturing process to produce mouldings of the present invention.

Another approach is to incorporate a hydrogenated cyclic polymer, for example a C₉ aromatic polymer, that is compatible with both the polyolefin bulk polymer of a blend and a cation exchanging layered silicate material such as clay and compounding the resultant mix at an appropriate temperature. Using an hydrogenated C₉ aromatic polymer as an example, the cation exchanging layered silicate material are added in roughly equal amounts. Preferably the cation exchanging silicate material is washed in water to remove impurities, and may advantageously be subsequently treated with a suitable quaternary cation such as a quaternary ammonium cation. An example of a suitable hydrogenated C₉ aromatic polymer is a polymer with the following formula:



Polymers conforming to the above formula are available from Arakawa Chemical Industries under the trade name ARKON. Other cyclic polymers containing unsaturated bonds, either within the cyclic group or in the polymer chain itself, will be suitable for the production of polyolefin organo-clay nanocomposites and may be determined by experimentation. One advantage of polymer/organo-clays manufactured using cyclic groups is that because they preferably have cyclic groups within them, they may well be particularly suitable as oxygen scavengers, particularly when compounded with catalysts capable of catalysing the oxidation of the cyclic and/or unsaturated functional groups. It is known that many oxygen scavengers containing cyclic groups produce fewer by-products than linear oxygen scavengers and which can migrate and thereby contaminate products packed into containers incorporating said oxygen scavengers. In such cases the polymer/organo-clay will perform the dual functions of a nanocomposite and oxygen scavenger (see Blends of the Present Invention).

Another method for preparing organo-clays capable of incorporation into polyolefins is to first functionalise the nanofiller with an aminosilane. Thereafter, a carboxylated or maleated polyolefin is grafted to the filler through an amine-carboxyl reaction. The resulting modified filler is dispersed in a semi-crystalline polyolefin (eg. polyethylene or polypropylene). Co-crystallization between the carboxylated or maleated polyolefin and the semi-crystalline polyolefin can improve interaction between the filler and semi-crystalline polyolefin.

Yet another method of preparing a polyolefin-compatible nanocomposite is to prepare an organophilic clay that is dispersible in non-polar organic solvents. The organophilic clay can then be treated with an alkyl aluminosilane and subsequently a catalyst, including Ziegler-Natta and metallocene catalysts, to form a complex that promotes olefin or styrenic polymerisation and platelet dispersion. The nanocomposite can be prepared directly by in situ polymerization of the olefin or the styrene at the nanofiller particles without shear, without an ion exchange step, and without the need to incorporate polar substituents into the polyolefin or polystyrene.

Another nanocomposite suitable for mouldings of the present invention consists of a non-polar bulk polymer such as polyethylene or polypropylene, an intercalated cation exchanging multi-layered silicate material such as an acid or quaternary ammonium treated montmorillonite or sepiolite clay, dispersed in the bulk polymer and an organic cation, such as polyethylene or polypropylene terminated by an amine group, the organic cation having a pendent polymer chain, the polymer of the pendent polymer chain being miscible with the bulk polymer. The nanocomposite material is made by blending the molten bulk polymer with the cation exchanging multi-layered silicate material and the organic cation.

It is well known that different intercalants result in different degrees of exfoliation; for example, octadecyl amine onium clay intercalant produces significantly better nylon-based nanocomposite barrier films compared to the same polymer

nanocomposite in which the clay intercalant is an n-alkyl dimethyl benzyl amine onium ion

Yet another beneficial and interesting nanoparticle suitable for use in a nanocomposite consists of an organic chemical/clay intercalate that has been ion-exchanged and reacted and intercalated with one-or-more quaternary ammonium compounds and an anionic material (such as sodium lauryl sulphate) which is further blended into a polymer resin to make a nanocomposite composition. This material can be blended into a wide variety of polymers. This kind of system disperses well in a number of different types of polymers, and has particular utility in non-polar polymers such as PE and PP.

Another type of intercalate consists of a functional organic monomer having at least one hydroxyl functionality and/or an aromatic ring. The intercalant monomer should preferably include an aromatic ring and/or have a hydroxyl or polyhydroxyl functionality to be sufficiently bound to the clay platelets. Such bonding, via a metal cation of the clay sharing electrons with electronegative atoms of one or two hydroxyl or aromatic ring structures, to an inner surface of the phyllosilicate platelets provides adherence between the intercalant monomer molecules and the platelet inner surfaces of the layered material, and the clay is subsequently exfoliated by processing with a polymer, preferably a polyolefin polymer, and if appropriate, a compatibiliser such as a maleic anhydride-modified polyolefin of the same type as the bulk polymer.

Yet another nanocomposite composition is prepared by co-intercalation of onium ions and an anhydride-curable epoxy resin. The ion-exchange binding between the onium ions and the platelet surface, via ion-exchange with intergallery inorganic cations, eliminates the presence of water molecules associated with the inorganic cations. Therefore, the onium ion-exchange enables the conversion of the hydrophilic interior clay surface to hydrophobic and, therefore, hydrophobic epoxy polymer molecules can then be intercalated into the clay galleries to increase the d-spacing of adjacent layers. The epoxy may, if appropriate, be reacted with a suitable epoxy curing agent added to the bulk polymer, which in turn will assist with the exfoliation when suitably compounded and may further improve the barrier properties of the nanocomposite thus formed as well as improve the adhesion of CVD and traditional varnishes/lacquers to the tube.

Another interesting synergistic intercalant combination consists of a long chain alkyl intercalant and/or an aromatic ring-containing intercalant, both having an electrostatic functionality at a layered material-complexed end of the molecule that is sufficient to provide electrostatic complexing of the intercalant to the interlayer cations on the platelet surface of the layered material, and a matrix polymer-compatible functionality extending from the intercalant molecule or at a free end thereof of the intercalant. Suitable long chain and aromatic ring-containing intercalants include a polar (electrostatic) end having at least one moiety selected from the group consisting of a hydroxyl functionality; a carbonyl functionality; a carboxylic acid or carboxylic acid salt functionality; an amine functionality; an amide functionality; an ether functionality; an ester functionality; a lactam functionality; a lactone functionality; an anhydride functionality; a nitrile functionality; an n-alkyl halide functionality; a pyridine functionality; a pyrrolidone functionality; a carbon-to-carbon unsaturated bond (i.e. an alkene or alkyne) and mixtures thereof to sorb or intercalate the intercalant or mixtures of intercalants between adjacent platelets of a layered inorganic material, e.g., a phyllosilicate.

Another interesting synergistic intercalant combination consists of an alkoxylated onium ion and EVOH. The use of this intercalant combination, and specifically the use of a polymer or other chemical group with good barrier properties that is compatible with the bulk polymer, frequently results in significant reductions in OTR of such nanocomposites relative to nanocomposites that don't have such good compatibility with the bulk polymer. Using intercalants that have good barrier properties (eg. EVOH) often results in nanocomposites with improved barrier properties relative to nanocomposites made with intercalants that don't have improved barrier properties. In the case of EVOH, the compatibility of the organo-nanoparticle with, for example, a PE bulk polymer can be improved through the use of EVOH with higher levels of ethylene copolymer; if the level of ethylene copolymer in the EVOH intercalant is high enough, the need for a compatibilising agent to form the nanocomposite may be reduced or even eliminated.

The amount of modified clay material combined with the polymers in a blend should be in an amount that is sufficient to provide the desired ESCR, barrier and/or mechanical properties. The amount of modified clay material in the nanocomposites is generally about 0.1% to about 25% by weight of the composition. A preferred range of modified clay material for tube production comprises about 0.5% to about 10% of the composition.

While certain clay minerals have been exemplified above it is understood that any clay mineral (both natural and synthesized) with a large contact area with the polymer to be used in said nanocomposite may be useful in tube production. Similarly it is understood that many fine, ultra-fine or nano-sized particle capable of forming a nanocomposite may be useful in the present invention, particularly if it acts as a nucleating agent for one or more of the polymers in the polymer blend.

To maximise the degree of exfoliation of any intercalated but not exfoliated galleries of the clay/organo-clay it is advantageous that the compound be subjected to very high shear rates during the manufacturing process.

RECENT POLYMER DEVELOPMENTS WITH UTILITY IN BLENDS OF THE PRESENT INVENTION

Highly Branched Polyolefin Developments

Recent developments in the production of highly-branched polyolefins have enabled the production of star, comb, nanogel and other similar polymers. These polymers feature a plurality of polyolefin arms linked to a polymeric backbone to provide a highly branched structure in which the properties of the highly branched structure can be conveniently tailored to the application for which the polymer is used. The choice of specific reactive polymeric backbone and/or its manner of preparation controls the branched structure as to comb, star, nanogel or structural combinations thereof. That allows for the preparation of polymers having relatively low viscosities compared to their linear counterparts at the same absolute molecular weight. These polymer types and blends made therefrom may be particularly suitable for the production of mouldings of the present invention. The rheological behaviour of these polymers with controlled branching shows surprising and useful features. These polymers frequently have a zero-shear viscosity that is larger than a linear polymer of the same molecular weight. They show a rapid drop in viscosity with shear rate (large degree of shear thinning) and a plateau modulus that is at least two times lower than that of

prior art linear and branched polymers. This latter characteristic is especially surprising, since ethylene polymers of various types exhibit essentially the same plateau modulus. This was thought to be intrinsic to the monomer type and not dependent on polymer architecture. The lower plateau modulus means that the comb and similar polymers are much less entangled than the linears, thus giving them such low viscosity for their molecular weight. The utility of these properties of these polymers is that they have a very low viscosity for their molecular weights under melt processing conditions and so will process much more easily than the prior art polymers. Even when added in relatively small quantities to conventional blends suitable for mouldings of the present invention, they can significantly improve blend processability. US 6,355,757 and US 6,084,030 amongst other patents describe the production of polymers such as are described above, and are incorporated by reference.

The copolymers of the above and similar inventions have utility in blends suitable for the production of mouldings of the present invention, those blends comprising the branched copolymer of the inventions at a very wide range, but most often between 1-5%. Depending on the properties of a specific highly-branched polymer of the above inventions and the desired properties of a particular formulation, said polymer may be used as a component of the ALOP or ALOCA part of the composition of the present invention. Depending on their properties they may also be regarded as additives rather than components of the polymer portion of the present invention.

Polypropylene Developments

A development of particular interest in for blends of the present invention is the ability to make elastomeric PP homo and copolymers. This is usually achieved by altering the tacticity of the polymer by various means. Another useful development is the ability to produce low flex modulus PP α -olefin copolymers with relatively low percentages of α -olefin copolymers.

As examples of one of these recent developments are linear or branched isotactic olefin polymers, particularly polypropylene homopolymers or random copolymers which have a structure in which their tacticity varies within the range of between 25 and 60% of [mmmm] pentad concentration. This variation in tacticity is due to the statistic distribution of stereoscopic errors in the polymer chains. Such polymers are described in, amongst others, WO 01/27169 (P&G), WO 99/52955 (Rieger) and WO 99/52950 (Rieger), all of which are incorporated by reference. Similarly, propylene/ethylene copolymers of the types described in US 6525157 (ExxonMobil) are suitable for use in mouldings of the present invention. It is worth noting that propylene α -olefins in which the number of Cs in the α -olefin is >4 have particular utility for products requiring improved cold creep resistance relative to propylene α -olefins in which the number of Cs in the α -olefin is ≤ 4 .

Also suitable for use in blends of the present invention are linear or branched isotactic polymers having an arbitrary or rather regular sequence of isotactic and atactic blocks within the polymer molecules, such as are described in WO/99/29749 (ExxonMobil), which is incorporated by reference. WO/99/2949 describes a branched polyolefin having crystalline sidechains and an amorphous backbone wherein at least 90 mole percent of the side-chains are isotactic or syndiotactic polypropylene and at least 80 mole percent of the backbone is atactic polypropylene. They may have particular utility in blends as ALOCAs or ALOHMFCAs in blends in which the ALOP is a crystalline or semi-crystalline PP. This will be particularly the case when the polymer in question has a relatively low flex modulus, as they act to reduce the flex

modulus of the blend with a crystalline or semi-crystalline PP ALOP, thereby increasing the tear resistance decreasing the flex modulus and improving the impact resistance of the blend.

Polymers such as are described in the abovementioned P&G, Rieger and ExxonMobil patents may be used as the ALOP or as an ALOCA or ALOHMFCA and may have either narrow or broad molecular weight distribution. Polymers such as are described above are often particularly suited to the production of mouldings of the present invention relative to the equivalent polymers of higher tacticity because their relatively reduced tacticity results in polymers with reduced rigidity and increased flexibility and elasticity. If the polymer(s) is used as an ALOCA or ALOHMFCA, it is advantageous – though not necessary – that it is used in conjunction with an ALOP that is made from the same monomer(s) as the ALOCA or ALOHMFCA because this results in greater compatibility/stability between the polymer(s) as well as allowing for easier recycling of mouldings of the present invention produced from such blends. For example, if the polymer is a polypropylene homopolymer or copolymer with tacticity varying between 25 and 60% of [mmmm] pentad concentration, it can be blended with a polypropylene homopolymer or copolymer with a higher tacticity to produce blends suitable for use in mouldings of the present invention. Alternatively, these polymers may be used in conjunction with other polymers to form blends that are suitable for use in the manufacture mouldings of the present invention. For example, these polymers may be blended with polyethylenes and copolymers of different types, including LDPE, MDPE and HDPE, which in turn may be manufactured using a variety of different manufacturing techniques, catalysts and copolymers such as are described in the '255 patent.

Another recent development in polypropylene polymerisation technology with application for tube production is the ability to produce very flexible, soft and elastic polypropylene polymers with minor percentage of ethylene copolymer and essentially no diene. These polymers have limited crystallinity due to adjacent isotactic propylene units and have a relatively low melting point. They are generally devoid of any substantial intermolecular heterogeneity in tacticity and comonomer composition, and are substantially free of diene. They are also devoid of any substantial heterogeneity in intramolecular composition distribution. The ethylene copolymer includes lower limit of 5% by weight ethylene-derived units to an upper limit of 25% by weight ethylene-derived units. Within these ranges, these copolymers are mildly crystalline as measured by differential scanning calorimetry (DSC), and are exceptionally soft, while still retaining substantial tensile strength and elasticity. Such polymers are described in US 6,525,157, which is incorporated by reference.

Recent developments have resulted in the synthesis of partially atactic, partially isotactic polypropylene polymers which have elastomeric properties. It is believed that in these components each molecule consists of portions which are isotactic, and therefore crystallisable, while the other portions of the same polypropylene molecule are atactic and therefore amorphous. Such polymers are suitable for mouldings of the present invention, either as ALOPs, ALOCAs or ALOHMFCA, combinations thereof or in combination with other polymers, such as polyethylenes, polypropylenes and/or α -olefin copolymers thereof. Examples of these propylene homopolymers containing different levels of isotacticity in different portions of the molecule are described by in, amongst others, U.S. Patent 5,594,080, in Journal American Chemical Society (1995), Vol. 117, page 11586, and in the Journal American Chemical Society (1997), Vol. 119, page 3635. Similarly, Equistar have developed a catalyst system that produces polypropylene with an isotactic pentad (mmmm)

content within the range of about 10 mole % to about 70 mole % and which should be suitable for tube blends.

Depending on the properties of the specific polymer, PP polymers such as are described above may be utilised, in whole or in part, in the formulation types described in the section on blends of the present invention either as ALOPs, ALOCAs. Their precise utility in given formulations may be determined by experimentation.

Blends of the present invention containing scavengers

Blends of the present invention may contain both nanocomposites and scavengers of various descriptions, such as oxygen scavenging components. It has now been found that there is a significant synergistic effect between the nanocomposite and scavengers such as oxygen-scavenging components that result in blends with much better barrier properties than either the equivalent nanocomposite or oxygen scavenging composition on their own.

The incorporation of oxygen scavengers into nanocomposites significantly enhances the oxygen barrier properties of nanocomposites for a wide variety of applications, including films and other articles made by extrusion or casting, injection stretch, injection blow, thermoforming and other plastic manufacturing processes. The nanocomposite preferably forms the continuous phase of blends of the present invention. The development of nanocomposite/oxygen scavenger compositions of blends of the present invention is particularly, but not exclusively, suited to mouldings of the present invention where enhanced oxygen and other barrier properties are required. Virtually any blend of the present invention, irrespective of polymer types, may be modified to be made suitable for use in scavenging blends of various types. For example, polyamides such as the various nylon polymers, polyesters such as PET and PEN, polycarbonates and polyolefins and blends thereof are suited for blends of the present invention. Polyolefins of various types in particular, as well as polyester-based blends of the present invention, by virtue of their relatively low cost and easy processability, are advantageously used for mouldings of the present invention.

Although the following discussion uses mainly polyolefin nanocomposite/oxygen scavenger compositions as examples, it will be understood that the same principles apply to other polymer types that can be compounded to produce nanocomposite/oxygen scavenger blends. In the context of nanocomposite/oxygen scavenging discussions, the term 'polyolefin' may therefore be substituted by, for example, polyester, polyamide, etc.

There are many oxygen scavenging systems that are suitable for use in blends of the present invention. Some of these are described in the section on blends of the present invention, but other systems not described may also be suitable. The suitability of a particular system may be determined by experimentation, as may the optimum type of nanocomposite to be used in conjunction with a particular oxygen scavenger(s) in the invention. Various types of nanocomposites and various methods for their preparation are described in the section on blends of the present invention, but it will be understood that the types and methods described are non-limiting. The compositions may be prepared by a variety of means, such as by mixing the blend components under high shear mixing conditions or other means capable of producing an intimate mix, such as in a twin-screw extruder. The nanocomposite/oxygen scavenger blend may also be produced by first preparing a nanocomposite and then as a separate step compounding the oxygen scavenger into the nanocomposite.

Alternatively, the polymer/oxygen scavenger blend may be prepared and the organo-clay, or masterbatch thereof, subsequently compounded into the polymer/oxygen scavenger blend. Other means to achieve a well mixed blend will be apparent to those skilled in the art.

In another variation of blends of the present invention, by selecting appropriate intercalants for the preparation of the organo-clay component of the nanocomposite to be used in the nanocomposite/oxygen scavenger blend it is possible to use as the intercalant a molecule that can also act as an oxygen scavenger. This may be achieved by, for example, selecting as an intercalant an organic molecule that has oxygen scavenging properties or by grafting, polymerising or otherwise incorporating an oxygen scavenging functional group(s) onto a 'standard' (i.e. non-oxygen scavenging) intercalant. For example, polymers grafted or polymerised with polyene oligomers such as butadiene and/or other unsaturated olefins and/or other unsaturated oligomers such as unsaturated cyclic functionalities (eg. cyclohexanyl-containing monomers and oligomers) are frequently capable of reacting with oxygen, said reaction rate frequently being accelerated by the incorporation of suitable catalysts, in particular, transition metals. The optimum level of oxygen scavenging polyene and/or other oxygen scavenging oligomer that is incorporated into a polymer by various means may be determined by experimentation. The optimum level will be influenced by a number of factors, such as the moulding and other physical properties of a polymer or blend at different levels of oligomer incorporation, the degree of oxygen scavenging required by the end use, the activity of the oxygen scavenging component of the blend, the processing conditions required to make the moulded article, etc. Typically, though not necessarily, the oligomer will be present in a 0.1 to 12% range, preferably 2% to 8%.

Typical non-limiting formulations of the present invention

Note that for the purposes of the formulations described below the nanocomposite added to the formulations is expressed as the weight percent of dry nanoparticles, eg. as dry organo-clay. In most cases where there is an organo-clay component in a formulation there will also be a functionalised polymer (in the case of polyolefin blends, usually a functionalised polyolefin) in the formulation. The functionalised polymer and the organo-clay are advantageously precompounded, often with a minor percentage by weight of the ALOP, facilitate good exfoliation of the organo-clay and then added to the blend as a masterbatch. For the purposes of the generalised formula below, the functionalised polymer component of the blend is regarded as part of the weight percent ALOP component of the blend.

Generalised non-limiting formulation of the present invention consist of:

1. 35-99% of an ALOP, preferably a polyolefin ALOP, even more preferably an mPE ALOP, yet more preferably a polyethylene ALOP such as mPE together with an LD, MD and/or HDPE and most preferably a mix of LD, MD and/or HDPE together with an mPE with density between 0.85 and 0.97, preferably the mPE has a density between 0.85 and 0.92, yet more preferably a density between 0.855 and 0.89.
2. 1-60% of an ALOCA/ALOHMFCA, preferably a polyolefin ALOCA/ALOHMFCA, yet more preferably a polypropylene-based ALOCA/ALOHMFCA in which propylene constitutes >50% of the monomer units in the polymer, yet more preferably a polypropylene-based ALOCA/ALOHMFCA in which propylene constitutes >80% of the monomer units in the polymer and most preferably a propylene-based

ALOCA/ALOHMFCA in which propylene constitutes >90% of the monomer units in the polymer.

3. Optionally 0.1-25%, preferably 0.1-15% and most preferably 0.1-10% of one or more nanoparticles, preferably exfoliated organo-clay nanoparticles
4. Optionally a suitable quantity of compatibilising polymer into which the nanoparticles, preferably organo-clay nanoparticles, are compounded to aid exfoliation of the organo-clay particles and to compatibilise the organo-clay and the ALOP.
5. Optionally a suitable quantity of a scavenger capable of reacting/binding with chemical entities that are regarded as undesirable in terms of the application of the blend of the present invention.

Formulas 1-4 are some typical, no-limiting blends of the present invention

Formula 1

33% 100 MFI PP homo or copolymer
 33% 10 MFI HDPE
 24% 5 MFI 0.87 density mPE
 4% organo-clay
 6% functionalised 5 MFI 0.87 density mPE

Formula 2

40% 10 MFI PP homo or copolymer
 34% 5 MFI HDPE
 10% 5 MFI 0.865 density mPE
 6% organo-clay
 10% functionalised 5 MFI 0.87 density mPE

Formula 3

25% 100 MFI PP homo or copolymer
 33% 60 MFI LDPE
 32% 30 MFI 0.87 density mPE
 4% organo-clay
 6% functionalised 30 MFI 0.87 density mPE

Formula 4

33% 100 MFI PP homo or copolymer
 40% 10 MFI HDPE
 27% 5 MFI 0.87 density mPE

Summary of the Main Factors Effecting ESCR of Blends of the Present Invention

The following points are a guide to how changing some of the polymer parameters of blends will effect blend ESCR. Note that these points are presented as guides, not definitive 'set-in-concrete' pronouncements on blend formulation.

- ESCR decreases with increasing percentages of higher crystallinity ALOPs
- ESCR decreases with increasing MFIs of the ALOP(s).
- ESCR decreases with increasing crystallinity of the miscible polymer(s) and/or mPE ALOPs
- ESCR increases with increases in the number of carbon atoms in the copolymer(s) used in the polymerisation of the ALOP—particularly mPEs—and/or miscible polymer, eg. octene (C₈) copolymers tend to produce better

results than butene (C₄) copolymers

- ESCR increases with increasing comonomer percentage in the ALOP.
- ESCR increases with decreasing MFI (i.e. increasing MW) of the mPE as well as any miscible ALOP polymers.
- ESCR increases with increasing numbers of amorphous and semi-amorphous areas within the blend. This increase in amorphous/semi-amorphous areas can be achieved by, amongst other things, adding an ALOCA that has the ability to interact with the ALOP in such a way as to reduce the crystallinity of the ALOP at the interface with the ALOCA. Examples of such ALOCAs are various homo and copolymers of polypropylene.
- ESCR increases with increasing amounts of ALOCAs. For example, ESCR increases with increasing PP percentage.
- ESCR increases with increasing percentage of nanocomposite.

Additives for blends of the present invention

Polymer blends suitable for tubes may incorporate a variety of additives. Examples of additional additives include further polymers, nucleating agents, pigments, dyes, fillers, antioxidants, plasticisers, oils, UV protection, viscosity modifying agents, additives capable of reacting with or absorbing deleterious chemicals such as oxygen, mould release agents, anti-block agents and melt strength modifiers amongst others. The addition of between 0.5% and 3% of a low MW hydrogenated aliphatic resin such as poly (dicyclopentadiene) may reduce the normalised moisture vapour transmission and sometimes the O₂ transmission rate of the blend and articles made therefrom. Additives may be added to one-or-more components of the polymer blend or the polymer blend as a whole prior to moulding in order to modify its properties to suit specific applications or to achieve specific effects in the end product. Some or all of the components of the polymer blend may be prepared by mixing—preferably intense mixing—so as to produce a very fine dispersion of the individual components within the matrix, followed by extrusion and chopping of the resultant polymer blend to be used in the injection moulding process of the present invention. Alternatively, the polymer blend may be provided in its component form and subjected to mixing before and during the melting of the polymer blend in the present process. It may also be prepared by a reactor process, in which the various components of the blends are polymerised sequentially or in parallel in reactor(s) – this process frequently resulting in very fine dispersions that are unable to be obtained by other means. Polymer blends of the present invention may also incorporate a variety of other additives. Examples of additional additives include further polymers, pigments, dyes, fillers, antioxidants, plasticisers, UV protection, viscosity modifying agents, additives capable of reacting with or absorbing deleterious chemicals such as oxygen and other mould release agents and melt strength modifiers amongst others. These additives may be added to one or more components of the polymer blend or the polymer blend as a whole prior to moulding in order to modify its properties to suit specific applications or to achieve specific effects in the end product.

It is also possible to make blends of the present invention conducting by adding various additives, such as conducting polymers and/or fine metal particles, to the blends. Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

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